available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue of the International Symposium on Single-Atom Catalysis (ISSAC-2016))

Catalytic activities of single-atom catalysts for CO oxidation: Pt₁/FeO_x vs. Fe₁/FeO_x

Jinxia Liang^{a,b}, Xiaofeng Yang^{c,*}, Congqiao Xu^b, Tao Zhang^c, Jun Li^{b,#}^a Guizhou Provincial Key Laboratory of Computational Nano-Material Science, Guizhou Synergetic Innovation Center of Scientific Big Data for Advanced Manufacturing Technology, Guizhou Education University, Guiyang 550018, Guizhou, China^b Department of Chemistry and Key Laboratory of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Tsinghua University, Beijing 100084, China^c State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

ARTICLE INFO

Article history:

Received 29 May 2017

Accepted 26 June 2017

Published 5 September 2017

Keywords:

Single-atom catalyst

FeO_x substrate

Density functional theory

Heterogeneous catalysis

CO oxidation

ABSTRACT

An FeO_x-based Pt single-atom catalyst (SAC), Pt₁/FeO_x, has stimulated significant recent interest owing to its extraordinary activity toward CO oxidation. The concept of SAC has also been successfully extended to other FeO_x supported transition metal systems both experimentally and theoretically. However, the FeO_x substrate itself (denoted by Fe₁/FeO_x following the same nomenclature of Pt₁/FeO_x) as a typical transition metal oxide possesses a very low catalytic activity toward CO oxidation, although it can be viewed as Fe₁/FeO_x SAC. Here, to understand the catalytic mechanism of FeO_x-based SACs for CO oxidation, we have performed density functional theory calculations on Pt₁/FeO_x and Fe₁/FeO_x for CO oxidation to address the differences between these two SACs in terms of the catalytic mechanism of CO oxidation and the chemical behavior of the catalysts. Our calculation results indicated that the catalytic cycle of Fe₁/FeO_x is much more difficult to accomplish than that of SAC Pt₁/FeO_x because of a high activation barrier (1.09 eV) for regeneration of the oxygen vacancy formed when the second CO₂ molecule desorbs from the surface. Moreover, density of states and Bader charge analysis revealed differences in the catalytic performance for CO oxidation by the SACs Fe₁/FeO_x and Pt₁/FeO_x. This work provides insights into the fundamental interactions between the single-atom Pt₁ and FeO_x substrate, and the exceptional catalytic performance of this system for CO oxidation.

© 2017, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Following the fabrication of the first practical single-atom catalyst (SAC), Pt₁/FeO_x [1], the concept of SACs has been successfully extended to other FeO_x supported metals, including

Ir₁/FeO_x [2,3], Au₁/FeO_x [2,4], and Ni₁/FeO_x [5]. Recently, considerable progress has also been made in the investigation of other single-atom catalysts [2,6–31]. These SACs possess well-defined surface-supported single-atom active sites, and exhibit high activity and stability in various heterogeneous

^{*} Corresponding author. Tel/Fax: +86-411-84379416; E-mail: yangxf2003@dicp.ac.cn[#] Corresponding author. Tel/Fax: +86-10-62795381; E-mail: junli@tsinghua.edu.cn

This work was supported by the National Natural Science Foundation of China (21503046, 21373206, 21203182), the National Basic Research Program of China (2013CB834603), the Natural Science Foundation of Guizhou Province of China (QKJ (2015)2122), Natural Science foundation of Department of Education of Guizhou Province (QJTD (2015)55 and ZDXK (2014)18), the GZEU startup package, the Open Fund of Shaanxi Key Laboratory of Catalysis to JXL (SXXLC-2017-01).

DOI: 10.1016/S1872-2067(17)62879-1 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 9, September 2017

reactions, including the water-gas shift (WGS), CO oxidation or preferential oxidation (PROX), and hydrogenation. Among these various reactions, CO oxidation is a simple yet important reaction, which has been extensively investigated from the perspective of environmental protection, exhaust purification for motor vehicles, gas purification for closed-cycle CO₂ lasers, and for CO detectors [32,33]. Moreover, this reaction is also an elementary step in the WGS reaction [2,34], and the preferential oxidation of CO in H₂ (i.e., the PROX reaction) serves as a key step for removing CO from reforming gas in fuel cell applications [35]. Over the past few decades, a number of oxide-supported noble-metals (e.g., Pt, Au, Ir, and Pd) [1,19,36–38] have been identified as active catalysts for CO oxidation. In particular, as for FeO_x based SACs, the supported non-noble 3d-transition metal has been even found to be effective for the oxidation of CO, that is, our recent theoretical investigation indicated that FeO_x supported 3d-transition metals such as Ni₁/FeO_x, can catalyze CO oxidation with high activity, even at room temperature [5].

While Fe is a typical 3d-transition metal and the Fe atoms in the FeO_x support can also be considered to be a monodisperse metal center on the surface of the support. To be consistent with the categorization of Pt₁/FeO_x SAC, here we denote the FeO_x substrate with an oxygen vacancy as Fe₁/FeO_x. However, this base material has been found to have a much lower activity for CO oxidation than that of Pt₁/FeO_x [1]. Our previous density functional theory (DFT) calculations showed that the high catalytic activity of Pt₁/FeO_x correlates with the partially vacant 5d orbitals of the positively charged, high-valence single-atom Pt₁. This effect reduces the probability of CO poisoning and facilitates adsorption of oxygen. However, it remains unclear what factors give Pt₁/FeO_x such a high catalytic activity [1] and limit the activity of the FeO_x support as a catalyst in CO oxidation. To understand the differences between these two catalysts, we performed theoretical investigations on possible catalytic reaction pathways of CO oxidation on Fe₁/FeO_x. We examined the chemical interactions using DFT, with our previous calculated results of Pt₁/FeO_x as a reference.

On the basis of our theoretical calculations, we show that among the fundamental differences in the catalytic activity toward CO oxidation between Pt₁/FeO_x and Fe₁/FeO_x, the regeneration of single-atom active centers is the key factor, which determines the catalytic activity for CO oxidation. These findings help to develop an understanding of the high activity of Pt₁/FeO_x for CO oxidation, which will guide the design of new FeO_x supported single-atom catalysts for potential practical applications.

2. Computational details

As used in our previous work [1], the (0001) surfaces of α -Fe₂O₃ were represented by a periodic slab model, constructed from bulk cell dimensions: $a = b = 5.04$ Å and $c = 13.72$ Å. Because α -Fe₂O₃ is antiferromagnetic and has an atomic magnetic moment on iron atoms, we used the primitive rhombohedral unit cell of Fe₂O₃ with a magnetic configuration (+ − +) to build the surface slab. This arrangement has previously been

shown to be the most energetically favored magnetic configuration for α -Fe₂O₃ [39]. A vacuum distance 12 Å-width in the direction perpendicular to the surface was set to eliminate the interaction between layered nanostructures in adjacent cells. Considering the large relaxation typical of Fe₂O₃ surfaces [1,40], we selected slabs containing 12 layers of Fe atoms, and 7 atomic layers of O₃ (see below) to model the O₃-terminated surfaces [1]. The 10 top-layer slabs of the surface were allowed to relax while the other layers beneath the surface were frozen during the geometry optimizations. On the basis of previous studies [1,8], here the relatively favorable O₃-terminated surface of Fe₂O₃ (0001) was selected, where each Fe₁ atom is coordinated by three surface oxygen atoms (i.e. the O₃ atoms), with a third-layer of Fe atoms lying below the Fe₁ atoms. The Fe₁ can be viewed as a single-atom adsorbed to the α -Fe₂O₃ substrate.

The theoretical calculations were performed by DFT using the Vienna Ab-initio Simulation Package (VASP) [41,42]. The core and valence electrons were represented by the projector augmented wave (PAW) [43] method and plane-wave basis functions with a kinetic energy cut-off of 400 eV [1]. Considering that both Pt and Fe have relativistic effects, we included the mass-velocity and Darwin relativistic effects through the PAW potentials. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) [44] exchange-correlation functional was used in the calculations. A Monkhorst-Pack grid of size of 3×3×1 was used to sample the surface Brillouin zone [1]. Ground-state atomic geometries were obtained by minimizing the forces on the atoms below 0.02 eV/Å. Because of the strong *d*-electron correlation effects for Fe, the calculations were performed with the DFT+U method, based on the formalism suggested by Liechtenstein and Dudarev et al. [45]. The parameters were set at $U = 4$ eV and $J = 1$ eV according to the previous study [1]. The transition states were obtained by relaxing the force below 0.05 eV/Å via the dimer method [46].

3. Results and discussion

3.1. Catalytic CO oxidation cycle on Fe₁/FeO_x catalyst

3.1.1. Formation of the first CO₂ molecule

We begin our study using the previous calculated model of M₁/FeO_x (M = Pt, Ir, Au, Ni) [1,3–5], which derives from the primitive structure of the α -Fe₂O₃ (0001) surface with an oxygen vacancy (O_{vac}) on its O-termination surface. The FeO_x substrate in this model is similar to other M₁ in M₁/FeO_x SACs with a single atom of Fe₁ anchored to the surface, denoted as Fe₁/FeO_x. After intensive searching for adsorption and transition states, the predicted catalytic cycle and calculated reaction energies of CO oxidation on the α -Fe₂O₃ substrate are shown in Fig. 1 (top view). The corresponding bond lengths of the species are presented in Fig. 2 (side view) and Table 1. In the initial step of the reaction (step i), an oxygen vacancy (O_{vac}) near the Fe atoms is constructed to represent the reduction of the hematite surface, and the optimized bond lengths Fe₁-O_{A1} and Fe₁-O_{A2} are found to be 1.78 and 1.77 Å, respectively. Owing to the presence of the oxygen vacancy, O₂ molecule prefers to dissociatively adsorb to the surface of FeO_x. That is, the calcu-

Fig. 1. Proposed reaction pathway for CO oxidation on the Fe₁/FeO_x catalyst starting from a surface with an oxygen vacancy (top view). O_{A1} (red) surface atom to the left of the single-atom Fe, O_{A2} (red) surface atom to the right of the single Fe, O_B atom (light green) above the adsorbed O₂, O_C atom (light green) at the bottom of the adsorbed O₂, O_D atom (dark green) of CO, C atom (pink) in CO and Fe atom (purple).

lated adsorption energy of O₂ dissociation (−3.75 eV) is much

higher than molecule activation of O₂ on the oxygen vacancy (−2.14 eV). With the dissociative adsorption of O₂ on the surface (step ii), the distance between the O_B atom (light green) and O_C atom (light green) is 2.70 Å (as seen Fig. 2), which indicates the formation of O adatoms on the surface. After this adsorption of O₂, the first CO molecule is co-adsorbed on the single-atom Fe₁ (step iii) through the C atom (pink) of CO, with a Fe–C distance of 2.18 Å. The optimized distance of the C and O_B atoms on the single-atom Fe₁ is 2.36 Å. As the C atom of CO approaches O_B to generate the first CO₂ molecule (CO + O_B → CO₂), only a negligibly barrier energy (0.08 eV) is needed to be overcome through the first transition state (TS-1) with an imaginary vibration frequency at 345i cm^{−1}. The activation barrier to the first formation of CO₂ on the single-atom Fe₁ is low enough for the reaction to occur at a relative low temperature. After climbing TS-1, the first CO₂ molecule desorbs from the surface of FeO_x, leaving behind the dissociated O_C atom to heal over the O_{vac} on the FeO_x surface (step iv).

In addition to reactions of CO_{ad} and O_{ad} on Fe₁ single active site through the Langmuir-Hinshelwood (L-H) mechanism, the Eley-Rideal (E-R) mechanism might also be involved in the catalytic process as suggested by our previous study on SAC Ir₁/FeO_x [3]. The E-R mechanism was also considered for formation of the first CO₂ on the Fe₁/FeO_x surface, owing to vertical adsorption of the dissociated O_B atom on the single-atom Fe₁. The calculated E-R reaction pathway and the selected distances of atoms in these species are presented in Fig. 3. The distance between the C atom of CO and the O_B atom vertically adsorbed on the single-atom Fe₁ is 3.33 Å, indicating only weak

Fig. 2. Structures of the species involved in the proposed reaction pathway for CO oxidation at the Fe₁/FeO_x catalyst site starting from the surface with oxygen vacancy (side view). See caption of Fig. 1.

Table 1

Comparison of energy evolution (eV) in the proposed reaction pathway for CO oxidation on Fe₁/FeO_x and Pt₁/FeO_x catalysts.

SAC	i	ii	iii	TS-1 ^b	iv	v	TS-2 ^b	vi	TS-3 ^b	vi-final
Pt ^a	0.0	−1.05	−2.32	−1.83(0.49)	−4.30	−5.38	—	−6.29	−5.50(0.79)	−6.49
Fe	0.0	−3.75	−3.55	−3.47(0.08)	−6.48	−7.21	−6.55(0.66)	−6.94	−5.85(1.09)	−6.56

^a Ref. [1]; ^b Energy barriers (eV) are listed in parenthesis.

Fig. 3. Proposed reaction pathway for formation of the first CO₂ molecule on the surface of the Fe₁/FeO_x catalyst via E-R mechanism. See caption of Fig. 1.

adsorption of the CO molecule in the initial reactant pattern (R), as shown in Fig. 3. By overcoming a barrier energy of 0.23 eV, the conversion of CO and O_B to CO₂ can be accomplished through a transition state (TS) on the surface of FeO_x to give the final product (P). Thus, both the L-H and E-R mechanisms might be involved in the formation of the first CO₂ molecule because the reaction activation energies of these two processes are low enough for the reaction of CO + O_B → CO₂ to occur at a low temperature.

3.1.2. Formation of the second CO₂ molecule

After the formation of a perfect Fe₁-terminated surface of α-Fe₂O₃ (0001) (step iv), the second CO molecule can favorably adsorb on the single-atom Fe₁ as illustrated in step v. The optimized adsorption energy of CO is −0.73 eV, and the distance between the C atom from CO and the O_C atom dissociated from O₂ is 3.11 Å, as shown in Figs. 1 and 2. The adsorbed CO can approach O_C at O_{vac}, leading to a small barrier energy of 0.66 eV for the reaction of CO + O_C → CO₂ via the L-H mechanism on the surface of FeO_x (TS-2). This transition state features an imaginary vibration frequency of 391i cm^{−1}. The distance between the C atom and O_C is shortened from 3.11 to 1.69 Å in TS-2, indicating the formation of a new C–O bond and the generation of a second CO₂ analogue on the surface of FeO_x; however, the CO₂ molecule remains adsorbed to the FeO_x surface (step vi). Before the CO₂ is released from the FeO_x surface into the gas phase, an energy barrier of 1.09 eV must be overcome in TS-3. Finally, the whole catalytic cycle for CO oxidation is complete and the original catalyst with O_{vac} (step i) of Fe₁/FeO_x is regenerated.

The reaction rate-determining step over the whole catalytic cycle is clearly the desorption of the second CO₂ molecule from the surface of FeO_x (TS-3). Thus, the FeO_x substrate without a supported single-atom Pt₁ has a much lower catalytic activity than that of Pt₁/FeO_x SAC in CO oxidation reaction, which agrees well with previous experimental results [1]. When the standard enthalpies of formation of the oxides are compared, the lower catalytic activity of Fe₁/FeO_x for CO oxidation is also likely related to the relatively high oxygen affinity of Fe (250–300 kJ/mol) [47].

3.2. Differences of M₁/FeO_x (M = Fe, Pt) catalysts for CO

oxidation

To determine why SAC Pt₁/FeO_x has a much higher catalytic activity than that of the substrate α-Fe₂O₃ (Fe₁/FeO_x), and elucidate the nature of the binding of the single-atom Pt₁ to the FeO_x support, we compared the mechanism of catalysis and electronic structures in the proposed reaction pathways of CO oxidation. The relative binding energies for CO oxidation over these two catalysts are presented in Table 1. As shown in Fig. 1 and Table 1, there are several differences between these two different catalysts. First, O₂ is adsorbed in a molecular form onto the single Pt₁ mechanism, but is dissociatively adsorbed on the single-atom Fe₁. Second, the difference in the mode of O₂ activation leads to a discrepancy in the energy barriers for formation of the first CO₂ molecules on Pt₁ and Fe₁ single-atom active sites. As shown in Figs. 1 and 2, the activation barrier for formation of the first CO₂ molecule on single-atom Fe₁ (0.07 eV, TS-1) is much lower than that on Pt₁ (0.59 eV, TS-1) because the dissociated O_B atom reacts with the adsorbed CO much more easily. Third, the activation barriers of the rate-determining step of these SACs for the second CO₂ formation are clearly different for the two SACs M₁/FeO_x (M = Fe, Pt). The activation energy of CO_{ad} + O_C → CO₂ (TS-3) on Pt₁/FeO_x (0.79 eV) is much lower than that of CO_{ad} + O_C → CO₂ (TS-3) on Fe₁/FeO_x (1.09 eV), indicating that the α-Fe₂O₃ substrate has a low catalytic activity for CO oxidation.

As seen from the calculated Bader charges for M₁ single-atoms in M₁/FeO_x (M = Fe, Pt) in Table 2, the valence electron loss of the Fe₁ single-atom (1.488 |e|) is larger than that of a single-atom Pt₁ species (1.045 |e|) after CO adsorption on these single atoms. This result indicates the different interaction strengths between the adsorbed CO molecules and the single atoms of Pt₁ and Fe₁. To further understand the chemical interactions between the CO molecule and Pt₁ or Fe₁ single-atoms, we analyzed the electronic properties of these two different surfaces before (step iv) and after (step v) CO adsorption. The formation of the second CO₂ molecule in these two steps governs the major differences in the process of CO oxidation. According to the density of states (DOS) distributions in Figs. 4 and 5, both the 3*d* and 5*d* states of the single Fe₁ and Pt₁

Table 2

Bond lengths, valence electron, and Bader charges for M₁ single-atoms in M₁/FeO_x (M = Fe, Pt) without oxygen vacancy (iv) and with CO adsorption on M₁ single-atoms (v) and M(OH)_x (x = 1–4) molecules in a cubic box of 20 Å × 20 Å × 20 Å.

Species	M–O bond length (Å)	Valence electron (M)	Bader charge of M (e)
Fe ₁ /FeO _x -v	1.810, 1.810, 1.810	6.512	1.488
Fe–OH	1.779	7.462	0.538
Fe–(OH) ₂	1.786, 1.786	6.851	1.149
Fe–(OH) ₃	1.816, 1.816, 1.816	6.484	1.516
Fe–(OH) ₄	1.791, 1.800, 1.798, 1.810	6.385	1.615
Pt ₁ /FeO _x -v	2.048, 2.034, 2.029	8.955	1.045
^a Pt–OH	1.877	9.765	0.235
^a Pt–(OH) ₂	1.870, 1.870	9.422	0.578
^a Pt–(OH) ₃	1.905, 1.919, 1.956	8.865	1.135
^a Pt–(OH) ₄	1.932, 1.936, 1.944, 1.940	8.735	1.265

^a Core electrons represented by ECPs, the Fe(*d⁷s¹*) and Pt(*d⁹p¹*) valence electron configurations are used in the calculations. ^a Ref. [4].

Fig. 4. Spin polarized density of states (DOS) of Fe-iv, Pt-iv and localized DOS projected on single-atom metals Fe₁ and Pt₁ and on O 2p orbitals of O atom surrounded by Fe₁ and Pt₁ single atoms in (a) and (b), respectively. The Fermi level is set at zero.

Fig. 5. Spin polarized density of states (DOS) of Fe-v, Pt-v and LDOS projected on single-atom metals Fe₁ and Pt₁, and on the C 2p orbitals of CO adsorption at the Fe₁ and Pt₁ single atoms in (a) and (b), respectively. The Fermi level is set at zero.

atoms mix well with the 2p states of the neighboring oxygen atoms, suggesting strong chemical interactions between the single metal atoms with the FeO_x support, and that the stability of Pt₁/FeO_x is equivalent to that of the FeO_x substrate. The C 2p states of the adsorbed CO also mix with the *d*-states of single-atom metal species, indicating chemical bonding of CO on both SACs. As shown in Table 1, the calculated CO adsorption energy on Pt₁/FeO_x is larger than that on the FeO_x substrate. From Fig. 2, the stronger CO adsorption on the Pt₁ center makes it easier for the adsorbed CO to bind to the surface O atom in the OC...O(surface) of **TS-3**. Indeed, for the **TS-3** structure the OC...O(surface) distance is 0.05 Å shorter for Pt₁/FeO_x than that for Fe₁/FeO_x, which accounts for the lower activation barrier of CO oxidation on Pt₁/FeO_x.

Finally, we use a (MeO)₃M←CO (M = Fe, Pt) molecular system to model the bonding interactions between CO and the single metal atom at the surface. In this model, the M atom is clearly in the +3-oxidation state, while the real oxidation states of Pt and Fe in Pt₁/FeO_x and FeO_x are likely to be somewhat different. However, this molecular model has a similar coordination environment to that of the surface Pt and Fe atoms, and can be used to provide insight into the orbital interactions involved at these types of active sites with similar local structure.

The structures optimized by the PBE functional and TZ2P basis sets as implemented in ADF 2016 are shown in Fig. 6 and the bond parameters are given in Table 3. The orbital energy-level correlation diagram is shown in Fig. 7, with the corresponding molecular orbitals listed in Table 4. As can be seen from Fig. 7 and Table 4, the 5σ orbital of CO is stabilized by a donor interaction with (MeO)₃M, and the main interactions in the frontier

Fig. 6. Optimized structures of (MeO)₃M←CO (M = Fe, Pt).

Table 3
Optimized structural parameters of (MeO)₃M←CO (M = Fe, Pt) (C_{3v}) at the PBE/TZ2P level of theory.

M	C-O/(Å)	M-C/(Å)	M-O/(Å)	∠O-M-O/(°)	∠Cco-M-O/(°)
Fe	1.166	1.689	1.805	115.3	102.8
Pt	1.154	1.945	1.918	116.2	101.4

Fig. 7. Energy-level correlation diagrams of molecular model systems. (a) $(\text{MeO})_3\text{Fe}\leftarrow\text{CO}$; (b) $(\text{MeO})_3\text{Pt}\leftarrow\text{CO}$.

MOs are back-donation to 2π orbitals of CO, which contribute to the HOMO-1 and LUMO+1 of $(\text{MeO})_3\text{Fe}\leftarrow\text{CO}$ as well as the HOMO-2 and LUMO of $(\text{MeO})_3\text{Pt}\leftarrow\text{CO}$. The calculated energy-level splittings between the bonding Fe $3d$ or Pt $5d$ and the anti-bonding orbitals CO ($2\pi^*$) of $(\text{MeO})_3\text{M}\leftarrow\text{CO}$ ($\text{M} = \text{Fe}, \text{Pt}$) are 4.73 and 5.24 eV, respectively. Thus, the orbital interactions between $2\pi(\text{CO})$ and $(\text{MeO})_3\text{Pt}$ are stronger than those between $2\pi(\text{CO})$ and $(\text{MeO})_3\text{Fe}$ owing to the larger extent of the Pt $5d$ orbital than that of the Fe $3d$. This effect cancels the lower energy of the $5d$ atomic orbitals (AOs) for Pt than that of the $3d$ orbitals for Fe. Therefore, the stronger adsorption of CO on the Pt single-atom active center and the higher activity of Pt_1/FeO_x for CO oxidation are related to differences in the orbital interactions between the various species and Pt $5d$ and Fe $3d$ orbitals.

4. Conclusions

We have performed systematic theoretical investigations using relativistic density functional theory (DFT) to develop an understanding of why single-atom Pt₁ on FeO_x possesses excellent catalytic activity for CO oxidation, but the FeO_x substrate alone is not an effective catalyst. Our calculations indicate that the formation mechanisms of the first CO₂ molecules on the surfaces of these SACs are quite different owing to the different activation of O₂ at these two single-atom sites. Molecular adsorption occurs on the single-atom Pt₁ while dissociative adsorption is unavoidable at the single-atom Fe₁. More importantly, a relatively high activation energy (1.09 eV) is required to remove the O atom from the perfect (0001) surface of $\alpha\text{-Fe}_2\text{O}_3$ through the formation of the second CO₂ molecule, owing to the weak $\text{Fe}(\text{OC}\dots\text{O}_{\text{surface}})$ interaction. A relatively high oxygen affinity for Fe (250–300 kJ/mol) and the weak strength of CO adsorption on the single-atom Fe₁ are the key factors contributing to the lower catalytic activity of Fe₁/FeO_x for CO oxidation. The present theoretical study offers an explanation for why the FeO_x support is effectively inert in CO oxidation compared with the SAC Pt₁/FeO_x. These findings provide in-

Table 4

MO contours of $(\text{MeO})_3\text{M}\leftarrow\text{CO}$ ($\text{M} = \text{Fe}, \text{Pt}$).

Molecular orbitals	$(\text{MeO})_3\text{Fe}\leftarrow\text{CO}$	Molecular orbitals	$(\text{MeO})_3\text{Pt}\leftarrow\text{CO}$
LUMO+1 12e		LUMO+1 14e	
LUMO 11a ₁		LUMO 13a ₁	
HOMO 11e		HOMO 13e	
HOMO-1 10e		HOMO-3 11e	
HOMO-10 8a ₁		HOMO-13 9a ₁	

Graphical Abstract

Chin. J. Catal., 2017, 38: 1566–1573 doi: 10.1016/S1872-2067(17)62879-1

Catalytic activities of single-atom catalysts for CO oxidation: Pt_1/FeO_x vs. Fe_1/FeO_x

Jinxia Liang, Xiaofeng Yang*, Congqiao Xu, Tao Zhang, Jun Li*
Guizhou Education University; Tsinghua University; Dalian Institute of Chemical Physics, Chinese Academy of Sciences

Pt_1/FeO_x has higher catalytic activity for CO oxidation than that of the FeO_x substrate alone because the regeneration of oxygen vacancies features a high activation barrier for desorption of a second CO_2 molecule at the surface of Fe_1/FeO_x (i.e., the FeO_x substrate).

sights that will be useful for the design of new FeO_x supported single-atom catalysts.

Acknowledgments

The calculations were done using supercomputers at Tsinghua National Laboratory for Information Science and Technology, the State Key Laboratory of Physical Chemistry of Solid Surfaces (Xiamen University), and Guizhou Provincial High-Performance Computing Center of Condensed Materials and Molecular Simulation.

References

- [1] B. T. Qiao, A. Q. Wang, X. F. Yang, L. F. Allard, Z. Jiang, Y. T. Cui, J. Y. Liu, J. Li, T. Zhang, *Nat. Chem.*, **2011**, 3, 634–641.
- [2] J. Lin, A. Q. Wang, B. T. Qiao, X. Y. Liu, X. F. Yang, X. D. Wang, J. X. Liang, J. Li, J. Y. Liu, T. Zhang, *J. Am. Chem. Soc.*, **2013**, 135, 15314–15317.
- [3] J. X. Liang, J. Lin, X. F. Yang, A. Q. Wang, B. T. Qiao, J. Y. Liu, T. Zhang, J. Li, *J. Phys. Chem. C*, **2014**, 118, 21945–21951.
- [4] B. T. Qiao, J. X. Liang, A. Q. Wang, C. Q. Xu, J. Li, T. Zhang, J. Y. Liu, *Nano Res.*, **2015**, 2913–2924.
- [5] J. X. Liang, X. F. Yang, A. Q. Wang, T. Zhang, J. Li, *Catal. Sci. Technol.*, **2016**, 6, 6886–6892.
- [6] J. X. Liang, Y. G. Wang, X. F. Yang, D. H. Xing, A. Q. Wang, T. Zhang, J. Li, in: R. A. Scott (ed.) *Encyclopedia of Inorganic and Bioinorganic Chemistry*, John Wiley & Sons, Inc., **2017**, 1–11.
- [7] Z. W. Huang, X. Gu, Q. Q. Cao, P. P. Hu, J. M. Hao, J. H. Li, X. F. Tang, *Angew. Chem. Int. Ed.*, **2012**, 151, 4198–4203.
- [8] L. Wang, S. R. Zhang, Y. Zhu, A. Patlolla, J. J. Shan, H. Yoshida, S. Takeda, A. I. Frenkel, F. Tao, *ACS Catal.*, **2013**, 3, 1011–1019.
- [9] J. H. Kwak, L. Kovarik, J. Szanyi, *ACS Catal.*, **2013**, 3, 2094–2100.
- [10] M. W. Chu, C. H. Chen, *ACS Nano*, **2013**, 7, 4700–4707.
- [11] H. T. Wang, Q. Feng, Y. C. Cheng, Y. B. Yao, Q. X. Wang, K. Li, U. Schwingenschlögl, X. X. Zhang, W. Yang, *J. Phys. Chem. C*, **2013**, 117, 4632–4638.
- [12] S. Lin, X. X. Ye, R. S. Johnson, H. Guo, *J. Phys. Chem. C*, **2013**, 117, 17319–17326.
- [13] S. H. Sun, G. X. Zhang, N. Gauquelin, N. Chen, J. G. Zhou, S. L. Yang, W. F. Chen, X. B. Meng, D. S. Geng, M. N. Banis, R. Y. Li, S. Y. Ye, S. Knights, G. A. Botton, T. K. Sham, X. L. Sun, *Sci. Rep.*, **2013**, 3, 1775.
- [14] M. Moses-DeBusk, M. Yoon, L. F. Allard, D. R. Mullins, Z. L. Wu, X. F. Yang, G. Veith, G. M. Stocks, C. K. Narula, *J. Am. Chem. Soc.*, **2013**, 135, 12634–12645.
- [15] Z. Guo, B. Liu, Q. H. Zhang, W. P. Deng, Y. Wang, Y. H. Yang, *Chem. Soc. Rev.*, **2014**, 43, 3480–3524.
- [16] J. Xing, J. F. Chen, Y. H. Li, W. T. Yuan, Y. Zhou, L. R. Zheng, H. F. Wang, P. Hu, Y. Wang, H. J. Zhao, Y. Wang, H. G. Yang, *Chem. Eur. J.*, **2014**, 20, 2138–2144.
- [17] M. Flytzani-Stephanopoulos, *Acc. Chem. Res.*, **2014**, 47, 783–792.
- [18] B. Long, Y. Tang, J. Li, *Nano Res.*, **2016**, 9, 3868–3880.
- [19] Y. G. Wang, Y. Yoon, V. A. Glezakou, J. Li, R. Rousseau, *J. Am. Chem. Soc.*, **2013**, 135, 10673–10683.
- [20] S. Back, J. Lim, N. Y. Kim, Y. H. Kim, Y. Jung, *Chem. Sci.*, **2017**, 8, 1090–1096.
- [21] B. T. Qiao, J. X. Liang, A. Q. Wang, J. Y. Liu, T. Zhang, *Chin. J. Catal.*, **2016**, 37, 1580–1586.
- [22] G. Y. Nie, P. Li, J. X. Liang, C. Zhu, *J. Theor. Comput. Chem.*, **2017**, 16, 1750013.
- [23] B. T. Qiao, J. X. Li, Y. G. Wang, Q. Q. Lin, X. Y. Liu, A. Q. Wang, J. Li, T. Zhang, J. Y. Liu, *ACS Catal.*, **2015**, 5, 6249–6254.
- [24] Y. G. Wang, D. H. Mei, V. A. Glezakou, J. Li, R. Rousseau, *Nat. Commun.*, **2015**, 6, 6511.
- [25] Y. Tang, S. Zhao, B. Long, J. C. Liu, J. Li, *J. Phys. Chem. C*, **2016**, 120, 17514–17526.
- [26] J. Liu, *ACS Catal.*, **2017**, 7, 34–59.
- [27] J. Lin, B. T. Qiao, N. Li, L. Li, X. C. Sun, J. Y. Liu, X. D. Wang, T. Zhang, *Chem. Commun.*, **2015**, 51, 7911–7914.
- [28] J. C. Liu, Y. G. Wang, J. Li, *J. Am. Chem. Soc.*, **2017**, 139, 6190–6199.
- [29] Y. Tang, Y. G. Wang, J. Li, *J. Phys. Chem. C*, **2017**, 121, 11281–11289.
- [30] Y. Tang, Y. G. Wang, J. X. Liang, J. Li, *Chin. J. Catal.*, **2017**, 38, DOI: 10.1016/S1872-2067(17)62829-8.
- [31] Q. Fu, Y. Luo, *J. Phys. Chem. C*, **2013**, 117, 14618–14624.
- [32] S. D. Gardner, G. B. Hoflund, B. T. Upchurch, D. R. Schryer, J. Schryer, *J. Catal.*, **1991**, 129, 114–120.
- [33] M. Haruta, *Catal. Today*, **1997**, 36, 153–166.
- [34] A. A. Gokhale, J. A. Dumesic, M. Mavrikakis, *J. Am. Chem. Soc.*, **2008**, 130, 1402–1414.
- [35] C. S. Song, *Catalysis Today*, **2002**, 77, 17–49.
- [36] S. Abbet, U. Heiz, H. Häkkinen, U. Landman, *Phys. Rev. Lett.*, **2001**, 86, 5950–5953.
- [37] M. Okumura, N. Masuyama, E. Konishi, S. Ichikawa, T. Akita, *J. Catal.*, **2002**, 208, 485–489.
- [38] Y. G. Wang, D. H. Mei, J. Li, R. Rousseau, *J. Phys. Chem. C*, **2013**, 117, 23082–23089.
- [39] L. M. Sandratskii, M. Uhl, J. Kübler, *J. Phys. Condens. Matter*, **1996**, 8, 983–989.
- [40] X. G. Wang, W. Weiss, S. K. Shaikhutdinov, M. Ritter, M. Petersen, F. Wagner, R. Schlögl, M. Scheffler, *Phys. Rev. Lett.*, **1998**, 81, 1038–1041.

- [41] G. Kresse, J. Hafner, *Phys. Rev. B*, **1993**, 47, 558–561.
[42] G. Kresse, D. Joubert, *Phys. Rev. B*, **1999**, 59, 1758–1775.
[43] P. E. Blöchl, *Phys. Rev. B*, **1994**, 50, 17953–17979.
[44] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, **1996**, 77, 3865–3868.
[45] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, Z. Szotek, W. M. Temmerman, A. P. Sutton, *Phys. Status Solidi A*, **1998**, 166, 429–443.
[46] G. Henkelman, H. Jonsson, *J. Chem. Phys.*, **1999**, 111, 7010–7022.
[47] C. T. Campbell, *Surf. Sci. Rep.*, **1997**, 27, 1–112.

单原子催化剂 M_1/FeO_x ($M = Pt, Fe$)的理论研究: CO氧化反应

梁锦霞^{a,b}, 杨小峰^{c,*}, 许聪俏^b, 张 涛^c, 李 隽^{b,#}

^a贵州师范学院贵州省纳米材料模拟与计算重点实验室科学云大数据开发及其产业应用协同创新中心, 贵州贵阳550018

^b清华大学化学系有机光电子与分子工程教育部重点实验室, 北京100084

^c中国科学院大连化学物理研究所催化基础国家重点实验室, 辽宁大连116023

摘要: 负载型纳米贵金属催化剂是用于多相催化反应的重要的催化剂之一, 也是各国催化科学与技术研发的重点, 其工业应用也越来越广泛。理论和实验的研究结果均表明, 当载体表面的金属粒子尺寸减小至亚纳米级乃至更小的低配位、不饱和的原子团簇时, 它们常常成为诱发催化反应的活性中心, 呈现更高的催化活性和选择性。将负载的金属尺寸由纳米量级减小至分散的金属团簇甚至单原子而使每个原子成为反应的活性位点已成为研究的重点。最近, 由张涛等首次合成的单原子催化剂(SAC) Pt_1/FeO_x 引起了国内外催化及表面科学工作者的极大关注。单原子催化剂作为连接均相催化剂和多相催化剂的桥梁, 不仅具有非均相催化剂的稳定、易于与反应体系分离、易表征等优点, 而且具有均相催化剂活性中心结构均一、活性中心原子利用率百分之百等优点。一方面, 单原子催化剂给多相催化领域注入了新的活力, 另一方面也更有利于运用量子与计算化学的研究方法建立与实验相匹配的理论模型并从原子水平上进一步理解多相催化反应的微观作用机理。

实验和理论的研究结果表明, 其它单原子催化剂如 Ir_1/FeO_x , Au_1/FeO_x 和 Ni_1/FeO_x 催化CO氧化反应表现出不同的活性。然而, 底物 FeO_x 中的Fe同样是第VIII族中的3d过渡金属, 却在低温下对CO氧化反应没有催化活性。我们围绕这一问题, 重点研究了底物 FeO_x 在负载单原子 Pt_1 前后催化CO氧化的反应机理和活性, 解释了单原子催化剂 Pt_1/FeO_x 相比于底物 FeO_x 为何具有如此高的催化活性的原因。我们采用Vienna Ab-initio Simulation Package (VASP)从头算模拟软件和密度泛函理论(DFT)的广义梯度近似(GGA)进行了理论计算。其中, 选择PBE泛函描述体系的交换关联相互作用, 用投影缀加波(PAW)赝势基组方法描述体系中的电子和离子实之间的相互作用, 对Fe原子采用了DFT+U方法进行d电子强相关校正, 并使用Dimer计算方法搜寻反应过渡态。

研究表明, 底物 FeO_x 中氧空位的再生伴随第二个 CO_2 分子从催化剂表面脱附的过程需要较高的活化势垒(1.09 eV), 这一过程是整个CO氧化反应的决速步。与此相比较, Pt_1/FeO_x 催化剂中, 由于Pt原子代替了表面Fe原子, 导致电子结构及性质的显著变化, 有利于CO的活化、氧化和 CO_2 的脱附。我们从电子能量态密度(DOS)和Bader电荷分析及模型分子团簇的轨道相互作用的角度进一步分析了两种催化剂存在差异的本质; 揭示了单原子催化剂 Pt_1/FeO_x 中 Pt_1 和底物 FeO_x 之间的相互作用的机理及催化剂表面Pt单原子在催化反应过程中的关键作用。

关键词: 单原子催化剂; 氧化铁载体; 密度泛函理论; 非均相催化; 一氧化碳氧化

收稿日期: 2017-05-29. 接受日期: 2017-06-26. 出版日期: 2017-09-05.

*通讯联系人. 电话/传真: (0411)84379416; 电子信箱: yangxf2003@dicp.ac.cn

#通讯联系人. 电话/传真: (010)62795381; 电子信箱: junli@mail.tsinghua.edu.cn

基金来源: 国家自然科学基金(21503046, 21373206, 21203182); 国家基础研究计划(2013CB834603); 贵州省自然科学基金(QKJ(2015)2122); 贵州省教育厅自然科学基金(QJTD (2015)55, ZDXK (2014)18); 贵州师范学院启动经费和陕西省催化重点实验室开放课题(SXKLC-2017-01).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).